compared with similar values of 2·6 and 9·2° found in α-resorcinol (Bacon & Jude, 1973).

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Hydrogen Bonding in $Ca(H_2PO_4)_2.H_2O$ as Determined by Neutron Diffraction*

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The hydrogen positions in $Ca(H_2PO_4)_2.H_2O$ have been determined and the structure refined to $R_w = 0·068$ and $R = 0·055$ using 1045 neutron data. No evidence is found for any disorder of the protons. The two crystallographically distinct $H_2PO_4^-$ ions are hydrogen bonded to each other and to the water molecule. The oxygen atom of the water coordinates to a calcium ion and a hydrogen atom from $H_2PO_4^-$ along its lone-pair orbital directions with distances $Ca\cdots O_w = 2·479$ Å and $H\cdots O_w = 1·679$ Å. One of the hydrogen atoms of the water molecule is 2·106 and 2·315 Å from two oxygen atoms, with $O_w–H\cdots O$ angles of 110·9 and 147·5°. The distances and angles indicate that only the stronger of these two interactions is structurally significant. The other hydrogen atom of the water molecule is involved in a hydrogen bond with $H_w\cdots O = 1·823$ Å and the angle $O_w–H\cdots O = 160·4°$.

Introduction

On the basis of a refinement of the structure of $Ca(H_2PO_4)_2.H_2O$ from X-ray diffractometer data, Dickens & Bowen (1971) located the hydrogen atoms approximately and calculated idealized positions. An electron-density difference synthesis based on the X-ray data suggested that one hydrogen bond involving the water molecule was bifurcated. Allowing each of the possible hydrogen bonds to be linear in turn gave rise to two possible idealized positions, which were, however, incompatible with the difference synthesis. However, disorder of the water molecule would be compatible with Berry's (1968) interpretation of the infrared spectrum of $Ca(H_2PO_4)_2.H_2O$.

We undertook a neutron-diffraction study in order to determine definitely the orientation of the water molecule and to establish the arrangement of hydrogen bonds formed by the water molecule.

Experimental

Crystals of $Ca(H_2PO_4)_2.H_2O$ were grown from solutions (Elmore & Farr, 1940). Most exhibited polysynthetic twinning, as is common for this material (Smith, Lehr & Brown, 1955), with (010) as the composition plane. A crystal was chosen whose twin components were approximately four-fifths and one-fifth of the total volume. The smaller component was removed by polishing the twin with pumice. The remaining part of the crystal was examined under a polarizing microscope to ensure that removal of the small component was complete. The resulting plate had dimensions $3 \times 5 \times 0·367$ mm (volume $\sim 5·5$ mm³) and was used for data collection after examination of the crystal by precession photography had shown no evidence of twinning. The cell constants, $a = 5·6261$ (5), $b = 11·889$ (2), $c = 6·473$ (8), $\alpha = 98·633$ (6), $\beta = 118·2$ (6), $\gamma = 83·344$ (6)°, are taken from Dickens & Bowen

(1971). 1486 unique reflections within a sphere defined by a neutron wavelength of 1·232 Å and a limiting 2θ of 100° were measured on a computer-controlled 4-circle diffractometer (Alperin & Prince, 1970) according to the procedure described by Prince (1972). Corrections for apparent absorption due to incoherent scattering of hydrogen were computed by the procedure described by Burnham (1966). The maximum and minimum transmission factors were 0·947 and 0·664, respectively.

Parameters for the calcium, phosphorus, and oxygen atoms as given by Dickens & Bowen (1971) were used to phase an F_o nuclear density synthesis that revealed all hydrogen positions. The scattering lengths (in units of 10^{-12} cm) used were Ca: 0·47, P: 0·51, O: 0·580 and H: 0·374 (Bacon 1972). Refinement of atomic parameters was accomplished with the program RFINE (Finger, 1968); the sum $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$, was minimized. The variance, σ^2, was the sum of that estimated from counting statistics and $0·006|F_o|^2$. Refinements including isotropic extinction led to agree-

ment indices $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0·06$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0·09$. At this stage many reflections apparently suffered from extinction effects and many with $|F_c| < 1·0 \times 10^{-12}$ cm (range of $|F_c|$ was 0·010 to 4·573) had $|F_o|$ values as much as 5 times greater than $|F_c|$. Subsequent cycles of refinement rejected those reflections for which the extinction coefficient was less than 0·65 (*i.e.* beyond the limit of the Zachariasen expression, Cooper & Rouse, 1971) or if $|F_c| < 1·0 \times 10^{-12}$ cm and $(|F_o| - |F_c|)/\sigma > 4·5$ (probability level of 10^{-5}). The refinement converged to $R = 0·055$ and $R_w = 0·068$ with an average shift-to-error ratio in the last cycle of 0·08. About 30 weak reflections and 150 strong reflections were rejected (15% of the observed data).*

The positional parameters did not differ significantly
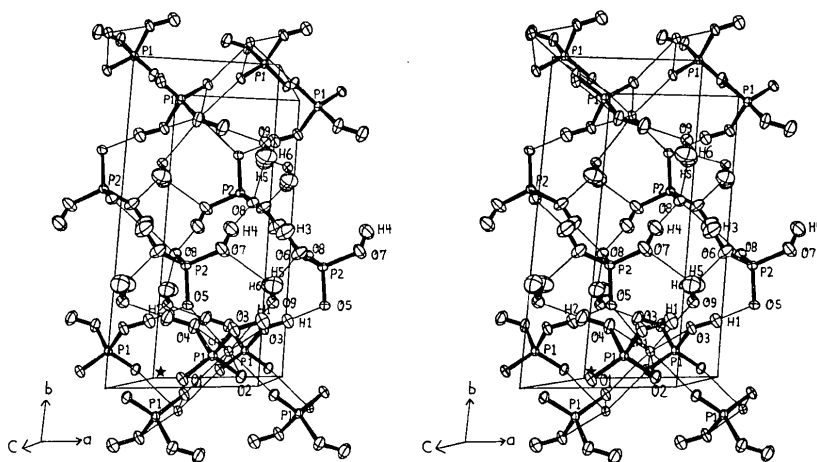
Fig. 1. A stereoscopic illustration of the crystal structure of $Ca(H_2PO_4)_2.H_2O$ based on the parameters determined from the neutron data. The water molecule is H(5)–O(9)–H(6). The origin of the coordinate system is marked by *.
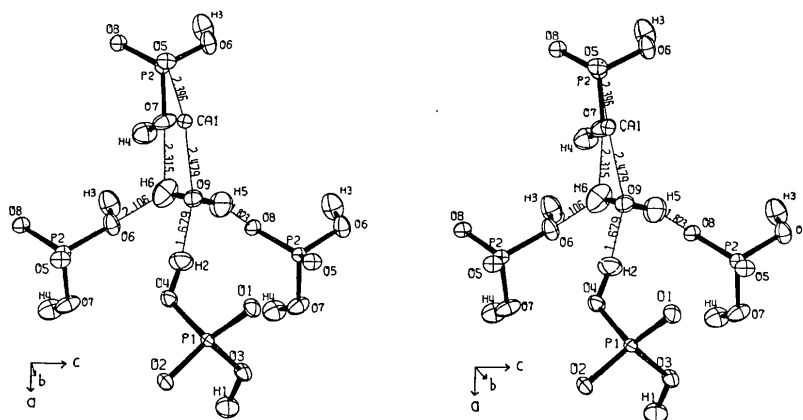

Fig. 2. The environment of the water molecule in $Ca(H_2PO_4)_2.H_2O$.

from the refinement of Dickens & Bowen but a few thermal parameters differed by three to four standard deviations. Only about 10% of the reflections with $I \leq 3\sigma(I)$ had $|F_c|$ values as large as $3\sigma(F_o)$ indicating that overestimation of $|F_c|$ was minimized. These reflections had zero weight in the refinements to ensure that reflections of moderate intensity determined the scale factor.

Plots of the least-squares residuals against $|F_c|^2/\sin 2\theta$ showed that $|F_c|$ values below 0·455 (the experimental threshold is ~0·410) were too large and those above 1·41 tended to be too small. Residuals lying between these limits did not show any variation with $|F_c|^2/\sin 2\theta$. Improvement of the fit would require a detailed analysis of the effect of simultaneous diffraction, but such an analysis is not warranted in view of the objectives of this study. The differences between structural parameters common to this study and the X-ray study are insignificant and show that a satisfactory refinement has been obtained here. Also, examination of Figs. 1 and 2 shows that all thermal parameters arereasonable in terms of the structure. The

largest feature in a difference synthesis of nuclear density was 1/10 of the height of the smallest atomic peak. The highest correlaticn coefficient was 0·79 between extinction and scale factors.

Results and discussion

Structural parameters are given in Table 1. Table 2 lists bond distances and angles that are significantly different from those obtained in the X-ray study. A thorough description of the structure has been given by Dickens & Bowen (1971) and our discussion here will center on hydrogen bonds.

The orientation of the water molecule is unusual. Both the results of the X-ray study and a calculation of the idealized hydrogen positions suggested that H(6) participates in a bifurcated hydrogen bond. Actually, the observation that the H(6)···O(6) distance is shorter than the H(6)···O(7) distance supports the contention that the former represents a stronger hydrogen bond, which results in P(2)–O(6) being longer than P(2)–O(7). The H(1)···O(5) distance of 1·584 Å is the shortest

Table 1. *Atomic parameters in* $Ca(H_2PO_4)_2 . H_2O$

The form of the thermal factor is $\exp[-2\pi^2(\sum_{ij}U_{ij}h_ih_ja_i^*a_j^*)]$. The figures in parentheses are standard deviations in the last significant digit as estimated by the last cycle of full-matrix least-squares refinement. U_{ij} for the H atoms are $\times 10^3$; all other values are $\times 10^4$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	7333 (4)	1028 (2)	7728 (3)	114 (9)	157 (9)	130 (9)	−23 (8)	51 (8)	18 (8)
P(1)	7458 (4)	975 (2)	2769 (3)	108 (9)	140 (9)	130 (9)	−3 (7)	60 (7)	25 (7)
P(2)	3486 (4)	3726 (2)	6129 (3)	159 (10)	116 (9)	193 (9)	−4 (7)	73 (7)	42 (8)
O(1)	5814 (4)	332 (2)	3406 (3)	166 (9)	203 (9)	181 (9)	−73 (7)	90 (7)	6 (7)
O(2)	9166 (4)	338 (2)	1730 (3)	162 (9)	214 (9)	184 (9)	27 (7)	113 (7)	36 (7)
O(3)	9212 (4)	1722 (2)	5149 (3)	180 (10)	242 (9)	191 (9)	−99 (8)	104 (7)	−48 (7)
O(4)	5646 (4)	1809 (2)	863 (3)	177 (10)	286 (10)	245 (9)	64 (8)	124 (7)	130 (8)
O(5)	3803 (4)	2455 (2)	6029 (3)	178 (9)	128 (9)	260 (9)	−10 (7)	83 (7)	44 (7)
O(6)	1903 (5)	4130 (2)	7590 (4)	401 (13)	267 (12)	346 (12)	105 (11)	264 (10)	101 (9)
O(7)	6349 (4)	4213 (2)	7571 (4)	228 (11)	292 (12)	354 (11)	−104 (9)	−3 (9)	140 (9)
O(8)	1990 (4)	4188 (2)	3759 (3)	212 (10)	185 (9)	226 (9)	8 (7)	8 (7)	7 (7)
O(9)	625 (4)	2525 (2)	−31 (3)	200 (10)	205 (10)	218 (10)	− 30 (7)	83 (7)	4 (9)
H(1)	1023 (7)	1955 (3)	5408 (6)	23 (2)	30 (2)	32 (2)	−8 (1)	10 (1)	6 (1)
H(2)	3814 (7)	2051 (3)	657 (6)	22 (2)	34 (2)	38 (2)	8 (1)	13 (1)	10 (2)
H(3)	702 (10)	4817 (4)	7140 (8)	58 (3)	35 (2)	57 (2)	12 (2)	40 (2)	11 (2)
H(4)	6745 (8)	4874 (3)	7047 (7)	33 (2)	32 (2)	46 (2)	−10 (2)	12 (2)	7 (2)
H(5)	855 (9)	3021 (4)	1390 (7)	45 (2)	42 (2)	36 (2)	−3 (2)	19 (2)	−6 (2)
H(6)	285 (10)	3064 (4)	8878 (8)	60 (3)	37 (2)	42 (2)	−4 (2)	15 (2)	12 (2)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *in* $Ca(H_2PO_4)_2 . H_2O$

i	j	k	D_{ij}	D_{ij}†	D_{jk}	D_{ik}	$\angle ijk$
H(5)	O(9)	H(6)	0·975 (5)	1·003 (5)	0·962 (5)	1·509 (5)	102·3 (4)
O(9)	H(5)	O(8)	0·975 (5)	1·003 (5)	1·823 (4)	2·761 (3)	160·4 (4)
O(9)	H(6)	O(6)	0·962 (5)	1·000 (5)	2·104 (5)	2·962 (3)	147·5 (4)
O(9)	H(6)	O(7)	0·962 (5)	1·000 (5)	2·315 (5)	2·916 (3)	119·9 (4)
O(3)	H(1)	O(5)	1·016 (4)	1·026 (4)	1·584 (4)	2·595(3)	172·5 (3)
P(1)	O(3)	H(1)	1·578 (2)		1·016 (4)	2·235 (4)	117·4 (3)
O(4)	H(2)	O(9)	0·987 (5)	1·000 (5)	1·679 (4)	2·622 (3)	172·3 (4)
P(1)	O(4)	H(2)	1·577 (2)		0·987 (5)	2·229 (4)	118·9 (3)
O(6)	H(3)	O(8)	0·983 (5)	1·000 (5)	1·728 (5)	2·694 (5)	166·4 (5)
P(2)	O(6)	H(3)	1·575 (2)		0·983 (5)	2·193 (3)	116·1 (3)
O(7)	H(4)	O(8)	0·987 (5)	0·991 (5)	1·653 (5)	2·626 (3)	167·5 (4)
P(2)	O(7)	H(4)	1·559 (3)		0·987 (5)	2·209 (5)	118·6 (3)

† D_{ij} after riding-model correction (Busing & Levy, 1964).

of the H$\cdots$O interactions and is consistent with the observation that O(5) accepts no other hydrogen bonds.

Since the publication of the X-ray study of Dickens & Bowen (1971) an important survey of 90 water molecules in over 40 hydrates studied by neutron diffraction has appeared (Ferraris & Franchini-Angela, 1972). It is interesting to examine the situation of the water molecule in $Ca(H_2PO_4)_2.H_2O$ in view of the distribution obtained in that survey. The water molecule in $Ca(H_2PO_4)_2.H_2O$ belongs to class $2H$, i.e. Ca and H(2) are coordinated at the positions of the lone-pair orbitals (see Fig. 2). A comparison of the H(6)$\cdots$O(8), H(6)$\cdots$O(6), and H(6)$\cdots$O(7) distances with the survey distributions shows the last to be an extreme value. The correlation of O_w–H and H$\cdots O_A$ distances in the survey shows that the limit of H$\cdots O_A$ distances is $\sim 2\cdot3$ Å. Corrections for the effect of thermal motion on O_w–H lengths might alter this slightly but the H(6)$\cdots$O(7) distance of 2·315 is still very long. A comparison of the angles O(9)–H(5)$\cdots$O(8), O(9)–H(6)$\cdots$O(6), and O(9)–H(6)$\cdots$O(7) (cf. Table 2) shows that they are all below the mean of the survey distribution. Although the distribution is skewed, as yet there are no examples with values as low as the O(9)–H(6)$\cdots$O(7) angle of 119·9°. In view of the observation that the distance and angle describing the O(9)–H(6)$\cdots$O(7) interaction are not as representative as the others, it cannot be considered on the same basis as the O(9)–H(6)$\cdots$O(6) bond. In our opinion the term 'bifurcation' implies that the proton is shared by the two accepted oxygens on a more or less equal basis and thus should not be used to describe the situation involving H(6) here.

The idealized positions calculated previously show that the water molecule can form fairly strong hydrogen bonds to either O(6) or O(7) alone. The real situation in $Ca(H_2PO_4)_2.H_2O$ can be understood in terms of electrostatic attraction from Ca and H(2) to the lone pairs of the water molecule, and both Ca$\cdots$H and H$\cdots$H repulsions; i.e. the present orientation seems to optimize Ca and H(2) interaction with the lone-pair orbitals while minimizing the Ca$\cdots$H(6) and H(6)$\cdots$H(2) repulsion energy. If the water molecule were rotated about the O(9)$\cdots$O(8) axis to make the O(9)–

H(6)$\cdots$O(6) angle $\sim 180°$, the H(6)$\cdots$H(2) distance would be less than 2·102 Å and the H(6)$\cdots$H(2) repulsion would be more significant. On the other hand, if the water were rotated about the O(9)$\cdots$O(8) axis so that the O(9)–H(6)$\cdots$O(7) angle approached 180°, the overlap of the lone-pair orbitals with the orbitals of Ca and H(2) would be less favorable and the Ca$\cdots$H(6) distance of 2·896 Å would decrease to $\sim 2\cdot48$ Å, which would increase the magnitude of this contribution to the repulsion energy.

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